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(56) Documents cited
GB 2180435 A GB 2166939 A GB 1042080 A
GB 0952658 A EP 0232672 A1 EP 0089762 A1
US 4750331 A US 4697508 A

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UK CL (Edition L) A2D DEF

(54) Freezing process and apparatus

(57) In a method of freezing a liquid-containing sample the heat extraction process is so controlled that each portion of the sample spends a predetermined time in the mushy zone (i.e. liquid and frozen solid together). In an embodiment of the invention, foodstuffs are cooled such that the mushy zone duration is less than 500 s, for soft fruit most preferably 100-300 s. In another embodiment the heat extraction rate is controlled so that the mushy zone duration is greater than 1000 s. Apparatus for carrying out the method may comprise a batch or tunnel freezer provided with means for controlling the temperature, mass and/or velocity of coolant gas supplied to the freezer.

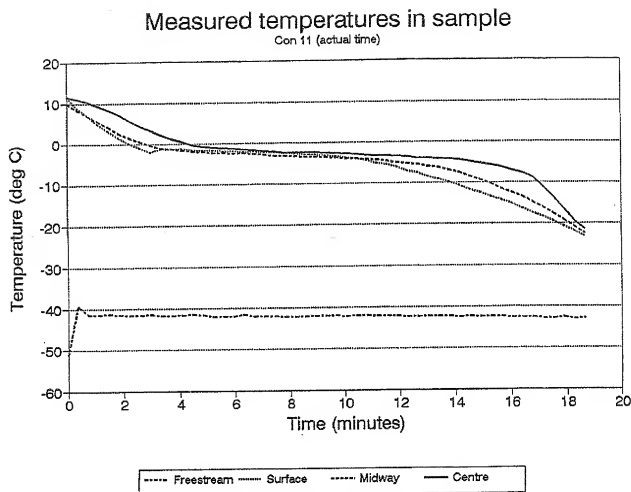


Figure 1.

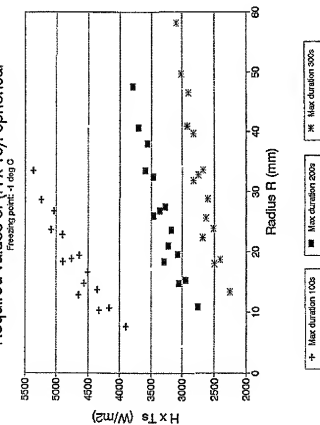
Required values of ($H \times Ts$): spherical

Figure 2a.

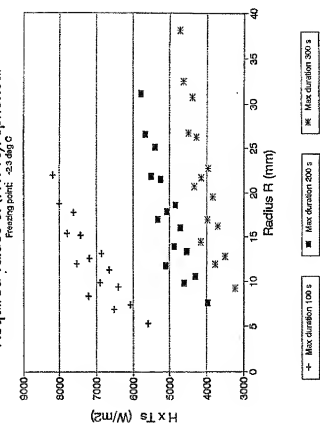
Required values of ($H \times Ts$): spherical

Figure 2b.

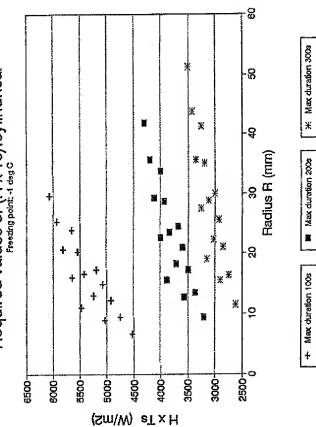
Required values of $(H \times Ts)$:cylindrical

Figure 3a.

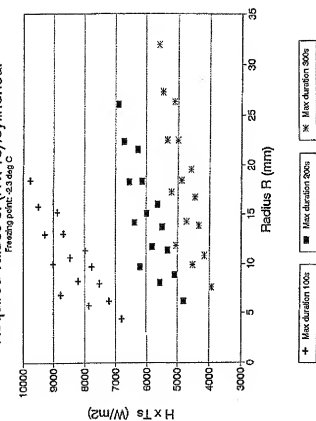
Required values of $(H \times Ts)$:cylindrical

Figure 3b.

Required values of (H x Ts): planar

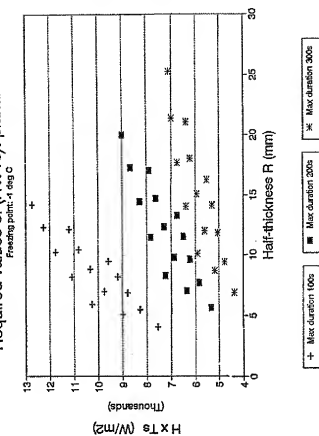


Figure 4a.

Required values of (H x Ts): planar

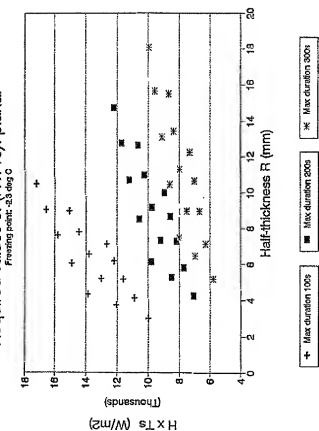


Figure 4b.

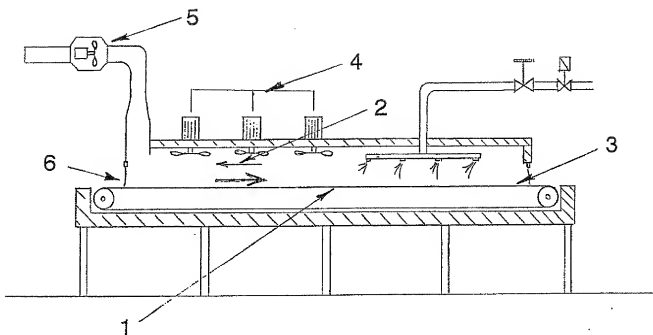


Figure 5.

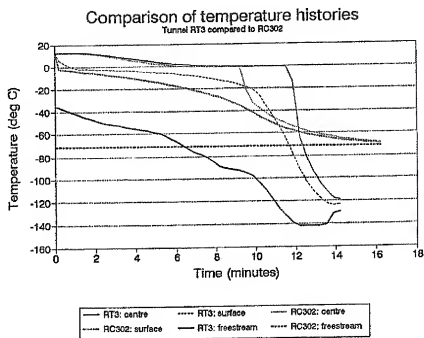


Figure 6.

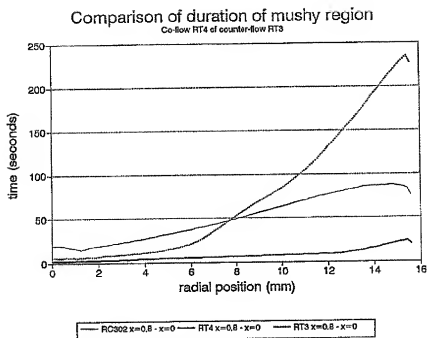


Figure 7.

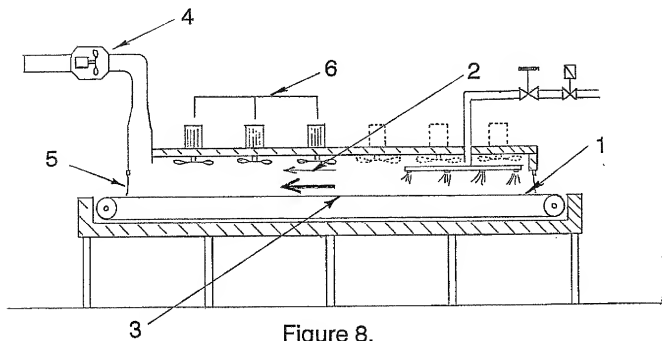


Figure 8.

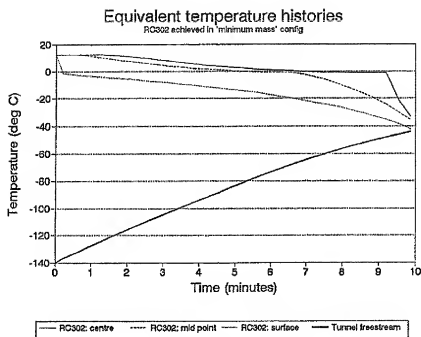


Figure 9.

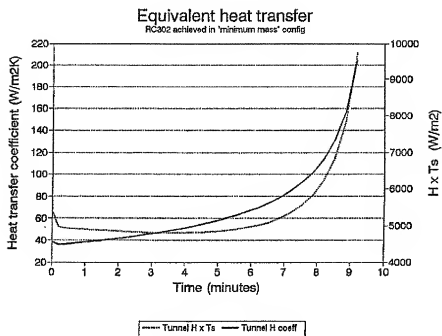


Figure 10.

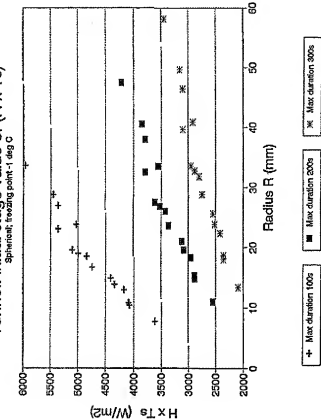
Tunnel: initial stage value of ($H \times Ts$)

Figure 11a.

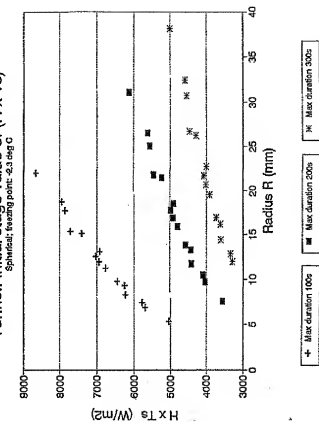
Tunnel: initial stage value of ($H \times Ts$)

Figure 11b.

Title - Process to control the freezing of foodstuffs.FIELD OF THE INVENTION

This invention relates to a method of controlling the freezing of foodstuffs and similar materials. The invention also relates to apparatus in which such processes are carried out.

The invention relates in particular to:

- (a) The freezing of foodstuffs which are generally consumed thawed, ie those generally recognised as 'frozen foods' including fruit, vegetables, meat, fish, bread, pasta, sauces, cooked or raw, natural or synthetic in origin, and any combination thereof.
- (b) The hardening step either of those products eaten in the frozen state, including ice cream, ices, sorbets, frozen yoghurt.. etc or processed for freeze drying, including coffee concentrate. The initial freezing step is usually carried out in a scrape surface heat exchanger so that approximately 50% of the available water is frozen, the product is then transferred to a second apparatus for hardening.
- (c) The use of freezing as a texturizing step for example in the processing of fish gels into Surimi (Chilling and Freezing of New Fish Products. International Institute of Refrigeration, Paris 1990).
- (d) The invention can also be applied to the freezing of tissues for purposes other than food including the preservation of flowers and other decorative materials, the cryopreservation of tissues and organs for medical and veterinary transplantation, the cryopreservation of aqueous suspensions, such as blood and bone marrow for transfusion and transplantation.

BACKGROUND TO THE INVENTIONA. THE PROBLEM

Whilst many foodstuffs may be adequately frozen using conventional food freezing techniques, in many cases such techniques are unsuccessful in producing high quality thawed material. Examples include many fruits such as strawberries, melons, mangos etc, vegetables such as potatoes, asparagus etc fish and crustacea, meats, pizze, gateaux, bread dough etc. Freezing damage to these various materials is manifest in a variety of undesirable

features. With sensitive fruit and vegetables extensive disruption occurs at the cellular level and thawed material demonstrates a loss of turgor (bite), discolouration, development of off-tastes, drip loss etc. With foods derived from animal and fish muscle, ie meat and fish, a toughening may also be apparent on thawing. In emulsions, including sauces such as mayonnaises, a separation of the constituents may occur on thawing. In flour based products such as breads staleness may develop, whilst pasta becomes tough.

One manner by which the food industry minimises the damaging effects of freezing in fruit and vegetables is to inactivate cellular enzymes before freezing by heating (Blanching). This process itself reduces product quality.

B. STATE OF THE ART RELATING TO THE INVENTION

(a) Current Understanding of the Freezing Process.

Many foodstuffs are tissues, ie collections of biological cells whose liquid, and therefore freezable, component comprises an aqueous solution. Other foodstuffs of interest are solely aqueous solutions, gels, suspensions or oil in water emulsions.

During freezing of aqueous systems, water is removed from the system as ice, and the concentration of the residual solution increases. As the temperature is lowered more ice forms decreasing the residual non-frozen fraction which increases in concentration. In aqueous solutions there exists a large temperature range in which ice co-exists with a concentrated solution, the so called 'mushy zone'.

The response of small volumes of cell suspensions during freezing and thawing are well understood (Mazur, 1963). However other phenomena are associated with the freezing of tissues and bulk fluids:

(i) Long exotherm. A typical temperature plot within a fruit (strawberry) during freezing is shown in Figure 1. The temperature within all of the material remains constant at approximately -2°C for some 500 secs even though the environment temperature is some 40°C colder. The core temperature remains constant at this temperature for a further 300 secs.

Similar temperature plots are observed during the freezing of bulk aqueous solutions, suspensions, gels and emulsions. It is commonly assumed that such temperature plateaux occur at the constant melting temperature whilst the 'latent heat' is being removed.

(ii) Site of Ice Formation. In bulk liquids, ice nucleation invariably occurs at the wall being cooled, as the 'latent heat' is removed crystal growth proceeds into the unfrozen material. In tissues there is little extracellular compartment making intracellular ice formation inevitable. It is only at very slow rates of cooling that the formation of ice in extracellular compartments leads to significant osmotic dehydration. However, even at these slow rates of cooling intracellular ice formation is probable. Such low rates of cooling are generally recognised to maximise cell damage in tissues and should be avoided.

The manner by which the various factors lead to damage during freezing, which is then expressed in terms of unacceptable product quality on thawing are not understood for tissues and bulk liquids. Some attempts relating the rate of freezing and damage on thawing have been made, however unlike the situation in cell suspensions no simple relationship exists.

(b) Current Food Freezing Equipment

A wide range of equipment is used to freeze foodstuffs (see for example Bek L, *The growth of the Frozen Food Freezing Industry Chapter 12 in Food Freezing: Today and Tomorrow*, Ed W B Bald, Springer-Verlag 1991): batch freezers where cold gas or cold contact plates are used to remove heat from the product, fluidised bed freezers, and tunnel freezers where the product is continuously fed through a cold gas tunnel. The source of refrigeration is either referred to as mechanical, when a gas usually air is cooled by a conventional refrigeration plant, or cryogenic when a liquefied gas such as liquid nitrogen, freon or carbon dioxide is used to produce the coolant gas. Direct immersion in liquid cryogens is employed in some specialised applications.

Whilst many of these freezing techniques are apparently designed to freeze sensitive materials as rapidly as possible, their lack of success in producing high quality material can be judged by the absence of commercially available material of freezing sensitive products.

STATEMENT OF INVENTION

According to the present invention in a method of freezing the heat extraction process is adapted so that each tissue compartment (ie cell, organelle) or zone of an aqueous sample spends a predetermined time in the 'mushy zone', the predetermined time being selected according to the type of material being frozen.

More particularly, in one aspect the invention provides a method of solidification by freezing of a sample of a substance incorporating at normal temperature and pressure a liquid phase, in which method the heat extraction process is so controlled that each portion of the sample spends a predetermined time in the temperature range within which solid, frozen liquid phase, material co-exists with liquid, unfrozen liquid phase, material (the so-called mushy zone), the predetermined mushy zone time being appropriate to the substance being frozen and being either below a critical value such that on subsequent thawing the substance shows no significant change in chosen physical characteristics or being above that critical value such that some such change does occur.

Where the freezing process is to preserve the foodstuff the method of the invention will normally require that the mushy zone duration is less than some critical value above which damage is found to occur.

Where the freezing process is to alter a characteristic of a foodstuff, such as texture, the control may be such as to ensure the duration of the mushy zone is greater than a given time.

The critical value above which damage is found to occur appears to be similar in many types of freezing-sensitive material, and is typically in the range of 50-750 seconds, and for soft fruit is typically in the range 100-300 seconds.

The invention may be achieved in many different ways, for example by controlling the flow (temperature, mass or velocity) of a coolant gas, direct immersion in a coolant liquid, contact with a cold solid, treatment under high pressure, and any combination thereof. Appropriate scaling for

different sizes of the same material and different compositions is given below. In general terms it is necessary to ensure that the convective cooling conditions are such that the magnitude of the product of the coolant temperature and the mean convective heat transfer coefficient is greater than specific values according to the size of the material being frozen and its composition. A detailed analysis of appropriate specific values and the desired control of the environment is given below.

Evidence of the need to control the duration of the mushy zone is demonstrated in the later section entitled Experimental Proofs.

A convenient definition of the mushy zone is that region in space or time between a volumetric ice fraction of zero and a volumetric ice fraction of 0.8. The temperature range over which this occurs increases with increasing molality and increased freezing point depression of the aqueous solution comprising the material to be frozen. For example for a material with a freezing point depression of 1°C , the mushy zone as defined above extends from -1°C to -4.45°C . For a material with a freezing point depression of 2.3°C the zone extends from -2.3°C to -12.6°C . This implies that faster cooling rates are required locally to prevent damage when the material has increased solute content due to ripening etc. This has been demonstrated experimentally and investigated further using a numerical model of the freezing process. To estimate the duration of the mushy zone at a point which the temperature has been measured during freezing it is only necessary to determine the freezing point of the material in order to calculate the molality, in order to define the appropriate temperature range corresponding to the mushy zone.

Measurements made on the strawberry data given in Experimental Proofs Series II show that in undamaged strawberries (of both high and low molality) the duration of the mushy zone was always less than 200s, in marginally damaged material it was 200-300s, and in severely damaged material it was in excess of 400s. Measurements of the duration of the mushy zone for a variety of materials are discussed in the section entitled Experimental Proofs Series II.

In summary, the benefit of the invention is that less cellular damage is caused by freezing. On thawing of material frozen by the method of the

invention the development of undesirable features associated with cellular freezing injury, including drip loss, discolouration, development of off-taste, are reduced or avoided. The invention significantly improves the quality of those materials which are currently frozen using conventional technology and allows the freezing, to a high standard of quality, of materials which previously could not be frozen commercially. An additional benefit of the invention is that by reducing cellular freezing injury, blanching of the starting material may not be required.

APPLICATIONS OF THE INVENTION.

Various examples of the use of the method of the invention are now described, though by way of illustration only, with respect to the following Examples and to the accompanying Drawings in which,

Figure 1 shows a typical temperature plot within a fruit during conventional freezing,

Figure 2 shows for spherical geometry the values of heat transfer parameters required to achieve the desired mushy zone duration,

Figure 3 shows for cylindrical geometry the values of heat transfer parameters required to achieve the desired mushy zone duration,

Figure 4 shows for planar geometry the values of heat transfer parameters required to achieve the desired mushy zone duration,

Figure 5 shows simplified form of conventional counter-flow freezing tunnel,

Figure 6 compares typical temperature profiles corresponding to freezing in a conventional freezing tunnel with desired profile,

Figure 7 compares calculated duration of the mushy zone for typical counter-flow tunnel with simple co-flow reversal,

Figure 8 shows simplified form of co-flow freezing tunnel,

Figure 9 shows tunnel temperature profile in "minimum mass" flow configuration,

Figure 10 shows heat transfer parameters corresponding to Figure 9,

Figure 11 shows for spherical geometry required values of heat transfer parameters derived from "minimum mass" configuration.

A. FREEZING IN A BATCH SYSTEM.

In a typical batch freezer (Air Products, mini-batch freezer), cooling is achieved by mixing cold gas either from a pressurised liquid vessel or a refrigerated source with air and circulating this around a sample chamber. Batch freezers are usually operated isothermally and it is assumed here that the method of control employed in these systems ensures that the presence of samples does not significantly modify the bulk gas temperature. The operating conditions may be modified by changing the speed of the fan(s) and/or the operating temperature. Changing the speed of the fan(s) changes the flow speed of the coolant gas and so changes the convective

heat transfer coefficient. (The relationship between local flow speed and heat transfer coefficient can be found in standard text books eg Introduction to Heat Transfer: Incropera F.P. & De Witt D.P., Wiley, 1985).

In order to constrain the duration of the mushy region to below any desired values it is necessary to ensure that the magnitude of the product ($H \times T_s$) is greater than certain appropriate values. (H is the average heat transfer coefficient (W/m^2K) and T_s is the temperature of the coolant gas, here defined for convenience in degrees Celsius below zero so that the product takes a positive value during freezing). The exact minimum value of ($H \times T_s$) is a function of Nusselt number, but it does not change significantly over the range of interest here.

Graphs have been produced for batch freezers using numerical modelling showing the relationship between the magnitude of the product ($H \times T_s$) and radius to achieve different mushy zone durations of 100, 200 and 300 seconds. Figure 2 shows the relationship where the material is generally in a spherical form, Figure 2a refers to materials having a freezing point of $-1^\circ C$ and Figure 2b to materials having a freezing point of $-2.3^\circ C$.

By selecting the appropriate set Figure 2a or Figure 2b the minimum ($H \times T_s$) value can be determined to achieve a maximum mushy zone duration of either 100, 200 or 300 seconds. Values for different mushy zone duration can be obtained if desired by interpolation and extrapolation.

Using strawberries (Chandler variety) of 15 mm equivalent mean radius (which can be assumed to approximate to spherical objects) and using a cooling arrangement achieving ($H \times T_s$) = 4900 (for example $-70^\circ C$ coolant temperature and a mean heat transfer coefficient of $70 W/m^2K$) successfully frozen strawberries can be obtained. Figure 2b predicts that the mushy zone duration in this case is of the order of 200 seconds.

The use of an alternative cooling system in which the same size of strawberry is used but the ($H \times T_s$) product is approximately 3,700, will result in a less satisfactory frozen strawberry (the mushy zone duration will be of the order of 300 seconds), but it is still superior to conventionally frozen strawberries.

No noticeable improvement was observed using the same size fruit and a more efficient cooling system having an $(H \times Ts)$ value of 7,500 for which Figure 2b predicts a maximum mushy zone duration of approximately 100 seconds.

It can therefore be concluded that an $(H \times Ts)$ value giving a predicted 200 second mushy zone duration is suitable for strawberries.

Further experiments have shown that the maximum mushy zone duration consistent with well frozen strawberries seems to be a constant value of the order of 200 seconds, irrespective of the size of the fruit and therefore Figure 2 can be used for strawberries in batch freezers.

Figure 3 relates to material generally in a cylindrical form; Figure 3a relates to material having a freezing point of -1° . -1°C is typical of vegetable material such as asparagus.

Using these graphs, experiments have shown that asparagus can be successfully frozen using an $(H \times Ts)$ value predicting a mushy zone duration of 100 seconds, but is not so successful when the $(H \times Ts)$ value is altered so as to correspond to a predicted duration of 200 seconds.

In the case of asparagus the mean radius is assumed to be typically 6mm and the shape generally cylindrical.

By adjusting the cooling system to give $(H \times Ts)$ values in between the two values for 100 and 200 and determining the frozen product quality, the minimum $(H \times Ts)$ value consistent with desired quality can be determined. As shown later, this will be found to be such as to give a 150 second mushy zone duration.

Figure 4 shows similar graphs for use with planar objects such as slices of meat, steaks, fish etc to give plots of $(H \times Ts)$ against mean cross-sectional half-thickness, for different mushy zone durations for use with batch freezers.

In the general case for any material which is either generally spherical or generally cylindrical or generally planar, the appropriate graphs are selected after determining the mean freezing point of the material, and if

the desired experiments can be performed using $(H \times T_s)$ values for the radius of the material concerned, commensurate with different mushy zone durations (of 100, 200 and 300 seconds for example), the best $(H \times T_s)$ value selected for subsequent processing of similar material after thawing and inspecting the material from different experiments.

Note that ripe fruit tends to have a higher solute (sugar) content than less ripe fruit. Where a range of ripeness is present, the freezing point of the riper fruit should be determined (or used, if known). In general, for fruit, the freezing point will normally lie in the range -1°C to -3°C and depending on the precise value, the appropriate set of graphs may be selected and used.

The thermal behaviour determined from Figures 4 - 6 can be achieved with a different coolant temperature T_g by allowing the convective heat transfer coefficient H to vary. The value of $h(t)$ when $T_s(t)$ is changed to $T_o(t)$ (say) is approximately given by: $h(t) = h(T_n(t) - T_s(t)) / (T_n(t) - T_o(t))$ where $T_n(t)$ is the (unchanged) surface temperature.

For the particular case where the desired surface temperature history is approximately linear, the new heat transfer coefficient corresponding to a different constant or linearly changing environmental temperature T_s is itself approximately constant. Otherwise the alternative distribution can be calculated numerically.

B. TUNNEL FREEZING.

In conventional tunnel freezers, food is generally passed through on a conveyor belt (1) in the opposite direction to the bulk flow of gas, (2) as illustrated in Figure 5. In this counter-flow system the food encounters the warmest gas as it first enters the tunnel at (6) and as it passes through, the temperature of the coolant gas decreases towards the exit (3). In typical cryogenic machines liquid nitrogen is sprayed into the tunnel near the exit and in some cases an adjacent fan (not shown) directs the cold gas into the tunnel. The coolant gas is mixed through these freezers by ceiling mounted variable speed fans (4) to a gas exhaust fan (5) at the product inlet (6), so that the gas exit temperature is typically -40°C , which is the temperature seen by the product on entry.

Taking an appropriate temperature profile for this tunnel and corresponding heat transfer coefficients (from Eek; Food freezing: Today and Tomorrow, 1991) an estimate can be made of the resultant freezing behaviour. Figure 6 compares the temperature histories of material present in the tunnel for 15 minutes (case RT3), with a constant temperature case RC302. Despite the lower final temperature the initial freezing is much slower resulting in a much increased duration of the mushy region in the outer part of the sample. Comparison of the input heat transfer coefficients of the two cases and the corresponding external heat transfer shows that whilst in RC302 the heat transfer during freezing is higher near the start of the freezing, in the tunnel case RT3 the heat transfer is lowest at the start, increasing only as the material passes through the most damaging region. As an illustration, a simple reversal of the tunnel, case RT4, remedies this with corresponding reduction of mushy zone as shown in Figure 7. (Although direct spraying with liquid nitrogen may be undesirable with some materials because of cracking etc, less violent contact with cold gaseous nitrogen only would be appropriate and allow control over the duration of the mushy zone.) This co-flow system is the most appropriate tunnel implementation to control efficiently the duration of the mushy zone within a product and this is discussed in detail below.

Control of duration of mushy zone using a co-flowing tunnel.

Example for freezing strawberries. A simple co-flowing nitrogen tunnel as sketched in Figure 8 would have a low inlet temperature at (1) corresponding to cold nitrogen vapour. The coolant co-flows (2) with the product as it travels on the conveyor belt (3) and would be heated by the product as the product freezes. The coolant exhaust (4) is now located near the product exit (5), mixing and appropriate convective effects being provided by the fans (6). A suitable temperature profile for a strawberry is shown in Figure 9 together with a possible corresponding temperature profile for the co-flowing coolant. With a constant belt speed, the temperature-distance curves for the bulk coolant temperature along the length of the tunnel can be derived from the coolant temperature - time curve in Figure 9 by multiplying the time along the axis by the belt speed. In the example shown here, the coolant inlet temperature is -140°C , and the calculated exit temperature of the product and coolant are close, with the coolant exhausting at approx -40°C . Figure 9 has been derived from a

numerical model of the freezing, and the heat transfer coefficient H corresponding to the increasing coolant temperature, T_s can also be calculated; this is shown in Figure 10. The curve marked 'Tunnel H coeff' represents the heat transfer coefficient that must be achieved in the tunnel to produce the temperature profiles in the strawberry shown in Figure 9 and the correspondingly short duration of the mushy region. It can be seen that the heat transfer coefficient rises rapidly towards the exit of the tunnel as the temperatures of the coolant and produce surface approach one another. This means that an increased local velocity is required, i.e. increased coolant movement must be generated eg by fans, as the product moves down the tunnel. The required flow speeds corresponding to these values of H may be estimated from standard text books as indicated above.

Towards the exit of the tunnel very high values of H may be required if, as specified in the example above, the coolant exit temperature is required to be close to the product exit temperature. This coolant flow may at this stage may be augmented by further addition of cold gas, spray of liquid nitrogen or a short immersion through a liquid coolant. For the case such as that given in the above example where there is no augmentation of the co-flowing coolant, it is possible to calculate the corresponding mass of coolant required to 'absorb' the heat from the freezing sample. When the final temperature of the coolant and the product surface are close as in this example, the calculated mass function corresponds to the minimum quantity of coolant that can freeze the material. We have defined the mass function to be mC_p/A where m/A is the mass of coolant per unit surface area of material being frozen and C_p is the specific heat (J/kgK) of the coolant gas. In this example we calculate (mC_p/A) to be equal to $24 kJ/m^2K$. This is a calculated minimum at this gas inlet temperature assuming no losses in heat transfer.

Figure 10 also shows the magnitude of the product $(H \times T_s)$ as a function of time. It can be seen that for a large part of the tunnel this has a value close to the value 4900 calculated in Figure 2b for a 15 mm radius sample in an isothermal environment with constant heat transfer coefficient.

This example has shown that the duration of the mushy zone can be constrained as required by freezing in a co-flowing nitrogen tunnel, with

coolant starting temperature -140°C and exit temperature close to -40°C . With a constant coolant mass co-flowing with the product, and exhausting with a temperature close to the product, an increase in mean heat transfer coefficient is an increase in local flow speed is required to achieve the necessary heat transfer when the temperatures of the product and the coolant approach one another.

Alternatively the necessary level of heat transfer can be achieved by later augmenting the coolant gas with lower temperature gas or liquid spray. Or the coolant mass flux could be increased above the minimum value so that the exhaust temperature was lower and further from the product temperature reducing the need for a high value of heat transfer coefficient. As the mass of coolant used increases the process resembles more closely a batch system throughout the tunnel and the heat transfer conditions defined in Figures 2-4 may be used.

Procedure for Calculating Co-flowing Tunnel Conditions.

Calculations using the numerical model have been made to show the temperature profiles and heat transfer coefficient requirements for a simple "minimum mass" co-flowing tunnel -140°C at inlet: these may be related to the desired duration of the mushy region in a similar way to the batch freezer discussed above.

The required "minimum mass" tunnel conditions have been derived numerically for different sizes of spherically shaped product as given below. To use these graphs it is necessary first to determine the freezing point and then determine optimum ($H \times T_s$) conditions to achieve acceptable frozen product. For soft fruit this will normally correspond to a mushy zone duration in the range 100 to 300s.

(i) Tunnel freezing of spherically shaped product, freezing point -1°C .

The appropriate values of ($H \times T_s$) of the initial stages of the tunnel for different sizes of material are given in Figure 11a for mushy region durations of 100s, 200s and 300s. These curves can be used to determine the required H from estimated values of coolant temperature or measured values in the tunnel. As explained above in the "minimum mass"

configuration, it is necessary to increase H , and substantially increase $(H \times T_s)$ as the freestream approaches the temperature of the product. The corresponding values of mass function (mCp/A) representing the estimated minimum coolant required per unit area of material being frozen can be assumed to vary linearly from 17 to 32.5 $\text{kJ/m}^2\text{K}$ over the radius range of each set of data points.

We may similarly present curves for:

(ii) Tunnel freezing of spherically shaped product, freezing point -2.3°C .

The appropriate values of $(H \times T_s)$ of the initial stages of the tunnel for different sizes of material are given in Figure 11b for mushy region durations of 100s, 200s and 300s. The corresponding values of minimum mass function (mCp/A) representing the estimated minimum coolant required per unit area of material being frozen, can be assumed to vary linearly from 15 to 30 $\text{kJ/m}^2\text{K}$ over the radius range of each set of data points.

With increased coolant mass and so lower coolant exit temperature, the product $(H \times T_s)$ will be approximately constant through the freezing, and given by Figure 11. These products are close to corresponding values given in Figure 2. It is therefore possible to apply measurements or calculations of $(H \times T_s)$ from one experimental configuration directly to any other experimental configuration. Further numerical calculations for cylindrical and planar geometry are unnecessary and the batch results for cylindrical and planar geometry given in figures 3 and 4 can be used to deduce tunnel conditions.

The desired effect, i.e. the control of the freezing process such that the time each tissue compartment or zone of an aqueous sample spends in the mushy zone is below the desired value, is determined by two interacting sets of variables:

(i) Variables relating to the starting material:

a) Precooling of the material to be as uniformly close as possible to the melting point is beneficial. However, in some material, for example potato, there is a enzymic conversion of starch to soluble sugars following

prolonged storage at low temperatures. This process, by leading to an increase in osmolality would be expected to result in increased tissue damage and so extended periods of low temperature storage prior to freezing should be avoided.

b) Post-harvest storage conditions and ripening treatments which result in recognised characteristics of ripeness together with a low solute content are beneficial. For example it is advantageous to use soft fruit such as strawberries which have been harvested unripe and ripened during transit with treatments such as ethylene.

c) Harvesting of material following cold stress, in particular with those vegetables which overwinter it is appropriate to harvest and process at their maximum intrinsic freezing tolerance.

d) Harvesting of material grown under conditions of osmotic stress such as drought or salt stress is beneficial.

(iii) Variables relating to the heat transfer from the freezing material to its environment.

The effect may be achieved in many different ways, in batch freezers or tunnel freezers, determined by chamber temperatures and heat transfer coefficients for any given size of material; the choice is determined by the freezing apparatus available.

a) In a batch freezer held at constant temperature, where the heat transfer coefficient may be controlled to be approximately constant, the graphs of products ($H \times T_s$), the heat transfer coefficients and environment temperatures, given in Figures 2 - 4 may be employed directly.

b) These data could also be used for a batch freezer with a constant environment temperature but variable heat transfer coefficients. This could be implemented in a batch freezer with suitable programmable fan control to modify the speed of a single fan, or control to allow the switching and speed control of multiple fans. The cooling gas being maintained at constant temperature by recoling in a refrigerated system and by replenishment as well or instead in a cryogenic system.

c) In tunnel freezers it is most appropriate to operate in a co-flowing configuration, with the warm food encountering the coldest gas or spray of liquid nitrogen. The gas flow is warmed as the frozen material cools. Figures 2, (11), 3, 4 give the estimated magnitude of the product ($H \times T_s$) to be realised in the tunnel. The coolant gas may flow straight

down the tunnel with the material, alternatively flow may be changed by fans, suitable section changes, baffles, plates etc into cross flow, downflow or upflow or any combination thereof as it travels in a general direction from one end to the other. The gas may be recirculated or replenished and additional sites for spraying with liquid nitrogen may be employed.

d) Tunnels employed in the counter-flow manner may also be arranged to operate in an appropriate manner to control the duration of the mushy region. Figures 2, 3, 4 again give appropriate values of $(H \cdot Ts)$ to be realised in the tunnel Gas flow and/or replenishment may be achieved by any of the methods described in (c).

e) Fluidised bed freezers may be considered to be a special case of a constant flow/constant temperature freezer. Where appropriate the heat transfer coefficients and environmental temperatures given in Figures 2 - 4 may be employed directly.

f) Where high values of heat transfer are required this can be achieved by spraying with cryogenic liquid provided that cracking does not occur.

g) Immersion in a liquid coolant such as Freon, liquid nitrogen or liquid CO_2 immersion often results in unacceptable fragmentation of the fruit, however, a short pre-dip followed by (a)-(e) may be beneficial. In addition during the continuous processing in methods (c) - (e), one or more immersion dips may be employed.

It will be understood that a combination of one or more of the above may also be of use in the method of the invention.

Control of the process may be achieved by direct temperature measurements on the products and the coolant gas flow during freezing, this data could be used to modify heat transfer coefficient as appropriate. Alternatively heat transfer may be determined by any other suitable method and data used to control the system.

In summary, successful freezing can be achieved simply by controlling the duration of the mushy zone. This can be checked by determining the melting point of the material and calculating the molality ($M_{pt}/1.86$) and so determining the temperature for the volume fraction $n = 0.8$. If the time

that any part of the sample spends between these temperatures is greater than the appropriate duration (eg 200s for soft fruit), damage will occur.

EXPERIMENTAL PROOFS

EXPERIMENTAL SERIES 1 - Proof of damage hypothesis.

We have suggested that the time a tissue compartment spends in the 'mushy zone' determines the extent of tissue damage on thawing. In material frozen under non-optimal conditions the peripheral part of the sample will be in the mushy zone for longer than the centre and it will thus be expected that there will be gradient of damage from the outside to the centre.

To examine this hypothesis, small onions (35mm max diameter) were frozen to a core temperature of -20°C in a flow of gaseous nitrogen/air at constant temperatures of -65°C . Following storage at -24°C for 24h the onions were thawed at air temperature. Onions were examined either cut in half or opened out into segments. This size of onion had 5 rings of tissue. The peripheral 2 rings of tissue were extensively damaged; compared to an unfrozen control they were translucent, had lost turgor and exhibited extensive drip loss. In contrast the inner two segments were similar to the unfrozen control. Temperature was monitored during freezing using T-type thermocouples (28 SWG) connected to a data logger, from these data it could be calculated that the duration of the mushy zone was 620s in the outer tissue and 120s in the centre. These observations clearly support our hypothesis of tissue damage during freezing.

EXPERIMENTAL SERIES 2

To determine the optimum method for freezing foodstuffs we have carried out a series of experiments in a batch freezing system.

The apparatus used for freezing was a Planar Kryo 10/16 cryogenic freezer (Planar Ltd, Sunbury-on-Thames, UK). Cooling is achieved by mixing cold nitrogen gas from a pressurised liquid vessel (0.5 Bar) with air and circulating this around a sample chamber (220 x 220 x 380 mm). The apparatus was operated isothermally and the method of control employed in this apparatus ensured that the presence of samples did not significantly modify the bulk gas temperature. The mean heat transfer coefficient at a

chamber temperature of -75°C was determined experimentally to be $50\text{ W/m}^2\text{K}$. Samples were placed on a wire rack 5cm from the bottom of the chamber, material was well spaced in a single layer. T-type thermocouples (28 SWG) were placed in the gas flow near to the sample, and at the centre, midway and just beneath the surface of the sample; thermocouples were connected to a data logger (Squirrel, Barrington, Cambs, UK). When the centre of the material reached -20°C the sample was transferred to a deep freeze operating at -24°C and stored for at least 24h. Unless otherwise stated material was thawed in the air at room temperature, typically $15\text{--}20^{\circ}\text{C}$. For comparison some material was also frozen in a commercial batch freezer (Frigoscandia).

The mushy zone duration was determined using the observed freezing point to calculate the tissue molality, which defines the appropriate temperature range corresponding to the mushy zone.

Strawberry: The conditions described here are for 13-14g strawberries (Chandler variety), which had been chilled to uniform temperature of approximately 10°C .

With a flow of gaseous nitrogen/air at constant temperatures of -65°C and below; at higher temperatures portions of the fruit exist in the mushy zone for excessive periods resulting in unacceptable product quality.

Following freezing by the method of the invention, strawberries were similar in taste, colour and texture to unfrozen material. The best results were obtained in material with a freezing point higher than -2°C . Experimental methods of freezing in which the duration in the mushy zone exceeded 300s within the material resulted in strawberries in which there was a loss of texture and significant drip loss. In commercially available material (Marks & Spencer) strawberries appeared pulp-like on thawing. The duration of the mushy zone was measured as 695 s during freezing in the Frigoscandia batch freezer set up to emulate commercial freezing processes.

Asparagus: The conditions described here are for unblanched asparagus tips 15 cm length with a maximum diameter of 1.5cm, typical weight 12-13g. The asparagus was successfully frozen as above with a flow of gaseous nitrogen/air at constant temperatures of -75°C and below. At higher

temperatures portions of the fruit existed in the mushy zone for excessive periods resulting in unacceptable product quality.

Asparagus frozen by the method of the invention were indistinguishable from unfrozen material, both in the cooked and uncooked states. Experimental methods of freezing in which the duration of the mushy zone exceeded 200s in any part of the asparagus resulted in product that did not retain turgor when thawed and on cooking tasted watery and fibrous. Commercially available frozen asparagus (Sainsbury) which had been blanched before freezing was of even poorer quality. Similar successful results were obtained following freezing of smaller asparagus (5-10mm diameter) a product commercially referred to as sprue.

New potatoes: The conditions described here are for unblanched potatoes, typical weight 25g, maximum dimensions 40mm. The product was chilled to uniform temperature of approximately 10°C before freezing.

Successful freezing of the product was achieved with a flow of gaseous nitrogen/air at constant temperature of -65°C. At lower temperatures excessive cracking of the product occurred, meaning that no further improvements could be made in this apparatus where only the chamber temperature was controllable. At higher gas temperatures product quality was unacceptable on thawing.

Potatoes frozen by the method of the invention were little changed in texture on thawing and when cooked they were very similar to unfrozen material. Experimental methods of freezing in which the duration of the mushy zone exceeded 500s in any part of the potato resulted a significant loss of texture and drip loss. Commercially available frozen potatoes (Sainsbury), which had been blanched before freezing, were unacceptably mushy when thawed out, on cooking from frozen some texture was retained but the product was 'soapy' in texture. Optimum results were obtained with 'waxy' varieties such as Charlotte, Belle de Fontenay and Pink Fir Apple; varieties such as Cara and Maris piper were less satisfactory.

Courgette: The conditions described here are for unblanched, unpeeled, crosswise slices (5mm thick) from courgettes 30mm in diameter, equilibrated to 4°C before freezing.

Successful freezing of the product was achieved with a flow of gaseous nitrogen/air at constant temperatures of -80°C and below. At higher temperatures portions of the fruit exist in the mushy zone for excessive periods resulting in unacceptable product quality.

Freezing by the method of the invention the courgettes were similar to unfrozen material. Following freezing by conventional methods a loss of turgor was observed together with extensive drip loss.

Pineapple: The conditions described here are for unpeeled, uncored, crosswise slices (1cm thick) and whole cored peeled pineapples, both were equilibrated to 4°C before freezing.

Successful freezing of the product was achieved with a flow of gaseous nitrogen/air at constant temperatures of -75°C and below. At higher temperatures portions of the fruit exist in the mushy zone for excessive periods resulting in unacceptable product quality.

Pineapple, both in slices and whole, frozen by the method of the invention was very similar in texture and taste to unfrozen material. The measured duration of the mushy zone in pineapple slices was less than 300 s. In pineapple slices frozen by standard methods the duration of the mushy zone was greater than 650 s and such material when thawed had an unsatisfactory drip loss, became pale on standing and tasted over-moist.

Mango: The conditions described here are for unpeeled, lengthwise, slices 7mm in thickness, which were equilibrated to 4°C before freezing.

Successful freezing of the product was achieved with a flow of gaseous nitrogen/air at constant temperatures of -90°C and below, under these conditions the duration of the mushy zone was less than 200 s. At higher temperatures portions of the fruit exist in the mushy zone for periods longer than 350 s, resulting in unacceptable product quality.

Mango slices frozen by the method of the invention retained their original texture, by contrast conventional freezing resulted in an unacceptable loss of texture.

Peach: The conditions described here are for unpeeled, lengthwise slices 3mm in thickness, which were equilibrated to 4°C before freezing.

Successful freezing of the product was achieved with a flow of gaseous nitrogen/air at constant temperatures of -75°C and below. At higher temperatures portions of the fruit exist in the mushy zone for excessive periods resulting in unacceptable product quality.

Kiwi Fruit: The conditions described here are for unpeeled, lengthwise slices, 4mm in thickness, which were equilibrated to 4°C before freezing.

Successful freezing of the product was achieved with a flow of gaseous nitrogen/air at constant temperatures of -75°C and below. At higher temperatures portions of the fruit exist in the mushy zone for periods greater than 300 s resulting in unacceptable product quality.

Sliced kiwi fruit frozen by conventional methods became dark green in colour, mushy in texture and exhibited a large amount of drip loss. Following freezing by the method of the invention the duration of the mushy zone was less than 200s, a brighter green colour was retained and there was little loss of texture or evidence of drip loss.

Cucumber: The conditions described here are for unpeeled, crosswise slices, 2mm in thickness, which were equilibrated to 4°C before freezing.

Successful freezing of the product was achieved with a flow of gaseous nitrogen/air at constant temperatures of -60°C and below. At higher temperatures portions of the fruit exist in the mushy zone for excessive periods resulting in unacceptable product quality.

Following conventional freezing sliced cucumber became translucent, lost turgor and exhibited significant drip loss. Using the method of the invention, cucumber slices were similar to unfrozen.

We have calculated/determined that to achieve acceptable quality on thawing of some sensitive fruit and vegetables it is necessary to ensure that the duration of the 'mushy zone' is less than 300s in all parts of the tissue

and in some cases less than 100s. We here demonstrate that this effect may be produced in a batch freezing system.

Prepared Meals: The conditions described here are for a freshly prepared meal consisting of chicken pieces and prepared vegetables in a sweet and sour sauce. 200g was placed in an aluminium tray (base dimensions 120mm x 95mm) and was equilibrated to 4°C before freezing. Following storage at -20°C the prepared meal was transferred directly to an oven at 160°C for 40 minutes.

Successful freezing of the product was achieved with a flow of gaseous nitrogen/air at a constant temperature of -110°C. The constituents of the meal frozen by the method of invention were little changed in texture compared with those in an unfrozen meal. The measured duration of the mushy zone in the prepared meal was less than 500 seconds. In prepared meals frozen by standard methods the duration of the mushy zone was greater than 1000 seconds and in such material when cooked a loss of turgor was observed in the vegetable constituents.

Pasta: The conditions described here are for freshly prepared Capatelli. Successful freezing was achieved with a flow of gaseous nitrogen/air at a constant temperature of -90°C. Following storage at -20°C the pasta was transferred directly to boiling water and cooked for 12 minutes. Pasta frozen by the method of the invention was very similar in texture and taste to unfrozen material. The measured duration of the mushy zone was less than 75 seconds. In pasta frozen by standard methods, the duration of the mushy zone was greater than 100 seconds and such material when cooked was considered to be tough.

EXPERIMENTAL SERIES 3 Removal of the requirement for blanching.

Belle de Fontenay Potatoes were frozen according to the method of the invention and following 3 months storage at -20°C material was thawed. Potatoes were little changed in texture on thawing and there was no evidence of the development of any off taste or any indication of browning. By contrast, unblanched potatoes frozen in a conventional manner were unacceptably discoloured following three months storage.

CLAIMS

1. A method of solidification by freezing of a sample of a substance incorporating at normal temperature and pressure a liquid phase, in which method the heat extraction process is so controlled that each portion of the sample spends a predetermined time in the temperature range within which solid, frozen liquid phase, material co-exists with liquid, unfrozen liquid phase, material (the so-called mushy zone),

the predetermined mushy zone time being appropriate to the substance being frozen and being either below a critical value such that on subsequent thawing the substance shows no significant change in chosen physical characteristics or being above that critical value such that some such change does occur.
2. A method as claimed in Claim 1, in which the heat extraction is effected by the passage around the sample of a coolant gas, and the temperature, mass and/or velocity of the coolant gas is/are controlled such that the product of the coolant temperature and mean convective heat transfer rate is appropriate to the material being frozen.
3. A method as claimed in Claim 2, in which the heat extraction process is effected within a batch freezer or a tunnel freezer.
4. A method as claimed in Claim 3 and using a tunnel freezer operated in a co-flowing configuration.
5. A method as claimed in any of the preceding Claims, in which, to obtain the required duration of the mushy zone:

there are determined the mushy zone boundary temperatures; and

there is then set and controlled the heat extraction rate such that there is attained the desired time within the mushy zone.

6. A method as claimed in Claim 5, in which, having first derived a set of Tables (Figures 2-4) defining the heat extraction conditions corresponding to predetermined mushy zone times for various chosen substances, and for various physical dimensions of samples of each such substance:

there is measured the freezing point of the substance's liquid phase, from which there is calculated the freezing point depression and thus the mushy zone boundary temperatures;

there are measured the physical dimensions of the substance sample; and

from the appropriate Figure there is selected a suitable product of coolant temperature and mean convective heat transfer coefficient necessary to obtain the desired mushy zone time.

7. A method as claimed in any of the preceding Claims, in which the sample is first pre-cooled to near liquid phase's freezing point.
8. A method as claimed in any of the preceding claims, in which the substance is a foodstuff, and to avoid altering the physical characteristics thereof the rate of heat extraction is such that the mushy zone duration is less than the critical value appropriate to that foodstuff.
9. A method as claimed in Claim 8, in which the duration of the mushy zone is less than 500 seconds.
10. A method as claimed in Claim 8, in which the substance is a soft fruit and the duration of the mushy zone is in the range 100 to 300 seconds.
11. A method as claimed in Claim 8, in which the substance is pasta and the duration of the mushy zone is in the range 25 to 75 seconds.
12. A method as claimed in any of the preceding Claims and substantially as hereinbefore described.

13. The use of a method as claimed in any of the preceding Claims for preserving the biological activity or viability of biological material.
14. A method as claimed in any of claims 1-7 which is used to control the texture of the sample substance for subsequent processing, in which the duration of the mushy zone is greater than 1000 seconds.
15. Apparatus for carrying out a solidification by freezing method as claimed in any of the preceding Claims, which apparatus comprises:

a freezing station, at which the sample to be frozen is brought into contact with a coolant gas;

means for supplying a flow of said coolant gas to the freezing station; and

means to control the temperature, mass and/or velocity of the supplied coolant gas such that the product of the temperature and the mean convective heat transfer is appropriate for the substance being frozen.
16. Apparatus as claimed in Claim 15 and being either a batch freezer or a tunnel freezer.
17. Apparatus as claimed in Claim 16 and being a tunnel freezer operated in a co-flowing manner.
18. Apparatus as claimed in any of the preceding Claims and substantially as hereinbefore described.

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Relevant Technical fields

(i) UK CI (Edition L) A2D (DEF)

(ii) Int CI (Edition)

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Databases (see over)

(i) UK Patent Office

(ii)

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Documents considered relevant following a search in respect of claims 1-18

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	GB 2180435 A (FRISCO-FINDUS)	at least Claim 1
X	GB 2166939 A (DICKINSON)	at least Claim 1
X	GB 1042080 (FRIGOSCANDIA)	at least Claims 1 and 5
X	GB 952658 (BECKMANN)	at least Claim 1
X	EP 0232672 A1 (VITAL FORCE)	at least Claim 1
X	EP 0089762 A1 (PATENTSMITH)	at least Claim 15
X	US 4750331 (BARTHEMES)	at least Claim 15
X	US 4697508 (TALLAFUS)	at least Claims 1 and 15

Category	Identity of document and relevant passages	Relevant to claim(s)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

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